

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 May 2006 (26.05.2006)

PCT

(10) International Publication Number
WO 2006/053740 A1

(51) International Patent Classification:
C08L 23/06 (2006.01)

(21) International Application Number:
PCT/EP2005/012305

(22) International Filing Date:
17 November 2005 (17.11.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10 2004 055 587.7 18 November 2004 (18.11.2004) DE
60/633,338 3 December 2004 (03.12.2004) US

(71) Applicant (for all designated States except US): BASELL
POLYOLEFINE GMBH [DE/DE]; Brühler Strasse 60,
50389 Wesseling (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): VOGT, Heinz
[DE/DE]; Kurmainzer Strasse 49, 65929 Frankfurt (DE).
BERTHOLD, Joachim [DE/DE]; Am Flachsland 54,
65779 Kelkheim (DE).

(74) Common Representative: BASELL POLYOLE-
FINE GMBH; Intellectual Property, Industriepark
Höchst-E-413, 65926 Frankfurt (DE).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,
LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI,
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG,
SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US,
UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: POLYETHYLENE MOLDING COMPOSITION FOR EXTERNAL SHEATHING OF ELECTRIC CABLES

(57) Abstract: The invention relates to a polyethylene molding composition which has a multimodal molar mass distribution and is particularly suitable for producing external sheathing of electric or information transmission cables. The molding composition has a density at a temperature of 23°C in the range from 0.94 to 0.95 g/cm³ and an MFI₁₉₀₁₅ in the range from 1.2 to 2.1 dg/min. It comprises from 45 to 55% by weight of a low molecular weight ethylene homopolymer A, from 30 to 40% by weight of a high molecular weight copolymer B of ethylene and another olefin having from 4 to 8 carbon atoms and from 10 to 20% by weight of an ultra high molecular weight ethylene copolymer C. The invention also relates to an electric or information transmission cable having an external sheath of the polyethylene molding composition which has a thickness in the range from 0.2 to 3 cm.



WO 2006/053740 A1

Title: Polyethylene molding composition for external sheathing of electric cables

5 The present invention relates to a polyethylene (PE) molding composition which has a multimodal molar mass distribution and is particularly suitable for producing cable sheathing, and a process for preparing this molding composition in the presence of a catalytic system comprising a Ziegler catalyst and a
10 cocatalyst via a multistage reaction sequence comprising successive polymerization steps.

Polyethylene is widely used for industrial applications in which a material having a high mechanical strength and a high
15 resistance to thermooxidative degradation is required in order to ensure a long life even at elevated use temperatures. In addition, polyethylene has the particular advantages that it has good chemical resistance, it has a low intrinsic weight and it is a material which can easily be processed in the
20 melt.

PE-molding compositions for cable sheathing should accordingly possess the following important properties:

- Easy processability.
- 25 - Good resistance to weathering influences.
- Good thermal aging resistance.
- Ability to withstand high mechanical stresses and good abrasion resistance.
- Low permeability to water vapor and oxygen so as to avoid
30 corrosion of the metallic conductor or conductors.

WO 97/03124 describes a coating composition based on polyethylene which has a bimodal molar mass distribution. This coating composition is very suitable for producing external
35 sheathing for energy and information transmission cables,

which give the cables sheathed therewith improved durability in respect of corrosion, in respect of oxidative aging, in respect of weathering influences of all types and in respect of mechanical stresses.

5

Known polyethylene molding compositions having a unimodal molar mass distribution have disadvantages in terms of their processability, their environmental stress cracking resistance and their mechanical toughness. Compared to these, molding
10 compositions having a bimodal molar mass distribution represent a technical improvement. They are easier to process and at the same density have an improved environmental stress cracking resistance and a higher mechanical strength.

15 It was thus an object of the present invention to develop a polyethylene molding composition which retains good processability but when used as cable sheathing displays significant advantages in respect of environmental stress cracking resistance, resistance to mechanical stresses and
20 improved abrasion behavior for simpler laying and relatively low water vapor permeation and oxygen permeation.

This object is achieved by a molding composition of the generic type mentioned at the outset whose distinguishing
25 features are that it comprises from 45 to 55% by weight of a low molecular weight ethylene homopolymer A, from 30 to 40% by weight of a high molecular weight copolymer B of ethylene and another olefin having from 4 to 8 carbon atoms and from 10 to 20% by weight of an ultra high molecular weight ethylene
30 copolymer C, where all percentages are based on the total weight of the molding composition.

The invention further provides a process for preparing this molding composition in a cascaded suspension polymerization
35 and a defect-free external sheathing of energy and information

transmission cables comprising this molding composition and having excellent mechanical strength properties combined with high stiffness.

5 The polyethylene molding composition of the invention has a density at a temperature of 23°C in the range from 0.94 to 0.950 g/cm³ and a trimodal molar mass distribution. The high molecular weight copolymer B contains a proportion of further olefin monomer units having from 4 to 8 carbon atoms, namely
10 from 1 to 8% by weight. Examples of such comonomers are 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-pentene. The ultra high molecular weight ethylene copolymer C likewise contains one or more of the abovementioned comonomers in an amount in the range from 1 to 8% by weight.

15 Furthermore, the molding composition of the invention has a melt flow index in accordance with ISO 1133, expressed as MFI_{190/5}, in the range from 0.5 to 2.1 dg/min and a viscosity number VN_{overall}, measured in accordance with ISO/R 1191 in
20 decalin at a temperature of 135°C, in the range from 260 to 340 cm³/g, in particular from 280 to 320 cm³/g.

The trimodality as a measure of the position of the centers of gravity of the three individual molar mass distributions can
25 be described with the aid of the viscosity numbers VN in accordance with ISO/R 1191 of the polymers formed in the successive polymerization stages. Here, the band widths of the polymers formed in the individual reaction stages are as follows:

30 The viscosity number VN₁ measured on the polymer after the first polymerization stage is identical to the viscosity number VN_A of the low molecular weight polyethylene A and is, according to the invention, in the range from 50 to 90 cm³/g,
35 in particular in the range from 60 to 80 cm³/g.

The viscosity number VN_2 measured on the polymer after the second polymerization stage does not correspond to VN_B of the relatively high molecular weight polyethylene B formed in the second polymerization stage, but is instead the viscosity number of the mixture of polymer A plus polymer B. According to the invention, VN_2 is in the range from 260 to 320 cm^3/g .

The viscosity number VN_3 measured on the polymer after the third polymerization stage does not correspond to VN_C of the ultra high molecular weight copolymer C formed in the third polymerization stage, which can likewise be determined only mathematically, but is instead the viscosity number of the mixture of the polymer A, polymer B plus polymer C. According to the invention, VN_3 is in the range from 260 to 340 cm^3/g , in particular from 280 to 320 cm^3/g .

The polyethylene is obtained by polymerization of the monomers in suspension at temperatures in the range from 70 to 90°C, preferably from 75 to 90°C, a pressure in the range from 2 to 10 bar and in the presence of a highly active Ziegler catalyst composed of a transition metal compound and an organoaluminum compound. The polymerization is a three-stage polymerization, i.e. it is carried out in three successive stages, with the molar mass being regulated in each stage by means of added hydrogen.

Apart from the polyethylene, the polyethylene molding composition of the invention can further comprise additional additives. Such additives are, for example, heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, peroxide-decomposing compounds, basic costabilizers, in amounts of from 0 to 10% by weight, preferably from 0 to 5% by weight, and also carbon black, fillers, pigments, flame retardants, or combinations of these

in total amounts of from 0 to 50% by weight, based on the total weight of the mixture.

The molding composition of the invention is particularly useful for producing external sheathing of electric cables of all types, e.g. cables for the transmission of information or energy. Such cables usually comprise one or more metallic or nonmetallic conductors which can each be coated with an insulating layer. The cable sheath has the task of protecting the cable against damage by external influences, e.g. during laying, and is preferably applied by extrusion by firstly plasticizing the polyethylene molding composition in an extruder at temperatures in the range from 200 to 250°C and then extruding it through a suitable nozzle onto the cable surface and cooling it there.

The molding composition of the invention can be processed particularly well by the extrusion process to produce coatings and has a notched impact toughness (ISO) in the range from 8 to 14 kJ/m² and an environmental stress cracking resistance (ESCR) in the range > 200 h.

The notched impact toughness_{ISO} is measured at -30°C in accordance with ISO 179-1/1eA / DIN 53453. The dimensions of the specimen are 10 x 4 x 80 mm, and it is provided with a V-notch having an angle of 45°, a depth of 2 mm and a radius at the bottom of the notch of 0.25 mm.

The environmental stress cracking resistance (ESCR) of the molding composition of the invention is determined by an internal measurement method and is reported in h. This laboratory method is described by M. Fleißner in Kunststoffe 77 (1987), p. 45 ff, and corresponds to ISO/CD 16770 which is now valid. The publication shows that there is a relationship between the determination of slow crack growth in a creep test

on test rods having a circumferential notch and the brittle branch of the internal pressure test in accordance with ISO 1167. A shortening of the time to failure is achieved by shortening the crack initiation time by means of the notch (1.6 mm/razor blade) in ethylene glycol as medium inducing environmental stress cracking at a temperature of 80°C and a tensile stress of 3.5 MPa. The production of the specimens is carried out by sawing three test specimens having dimensions of 10 x 10 x 90 mm from a 10 mm thick pressed plate. The test specimens are in turn notched in the middle by means of a razor blade in a notching apparatus made in-house for this purpose (cf. figure 5 in the publication). The notch depth is 1.6 mm.

15 Example 1

The polymerization of ethylene was carried out in a continuous process in three reactors connected in series. A Ziegler catalyst which had been prepared by the method of WO 91/18934, example 2, and has the operations number 2.2 in the WO in an amount of 0.08 mmol/h and also sufficient suspension medium (hexane), triethylaluminum as cocatalyst in an amount of 0.08 mmol/h, ethylene and hydrogen were fed into the first reactor. The amount of ethylene (= 65 kg/h) and the amount of hydrogen (= 68 g/h) were set so that a proportion of from 25 to 26% by volume ethylene and a proportion of 65% by volume of hydrogen were measured in the gas space of the first reactor; the remainder was a mixture of nitrogen and vaporized suspension medium.

30

The polymerization in the first reactor was carried out at a temperature of 84°C.

The suspension from the first reactor was then passed to a second reactor in which the proportion of hydrogen in the gas

35

space had been reduced to 7 - 9% by volume and into which an amount of 48.1 kg/h of ethylene plus an amount of 2940 g/h of 1-butene were introduced. The reduction in the amount of hydrogen was achieved by means of H₂ intermediate

5 depressurization. 73% by volume of ethylene, 8% by volume of hydrogen and 0.82% by volume of 1-butene were measured in the gas space of the second reactor; the remainder was a mixture of nitrogen and vaporized suspension medium.

10 The polymerization in the second reactor was carried out at a temperature of 80°C.

The suspension from the second reactor was passed via a further H₂ intermediate depressurization, by means of which the

15 amount of hydrogen in the gas space in the third reactor was set to 2.5% by volume, into the third reactor.

An amount of 16.9 kg/h of ethylene plus an amount of 1500 g/h of 1-butene were introduced into the third reactor. A

20 proportion of ethylene of 87% by volume, a proportion of hydrogen of 2.5% by volume and a proportion of 1-butene of 1.2% by volume were measured in the gas space of the third reactor; the remainder was a mixture of nitrogen and vaporized suspension medium.

25

The polymerization in the third reactor was carried out at a temperature of 80°C.

The long-term activity of the polymerization catalyst

30 necessary for the above-described cascaded mode of operation was ensured by a specially developed Ziegler catalyst having the composition reported in the abovementioned WO document. A measure of the usability of this catalyst is its extremely high response to hydrogen and its high activity which remains

35 constant over a long period of from 1 to 8 hours.

The suspension medium is separated off from the polymer suspension leaving the third reactor, the powder is dried and the powder is passed to pelletization.

5 The viscosity numbers and the proportions W_A , W_B and W_C of polymers A, B and C for the PE molding composition prepared as described in example 1 are shown in table 1 below:

10 Table 1

Example	1
W_A [% by weight]	50
W_B [% by weight]	37
W_C [% by weight]	13
VN_1 [cm^3/g]	80
VN_2 [cm^3/g]	280
VN_{overall} [cm^3/g]	304
FNCT [h]	220
AFM (-30°C)	3.8 kJ/m^2
ACN ($+23^\circ\text{C}$)	13 kJ/m^2

15 The abbreviations for the physical properties in table 1 have the following meaning:

- FNCT = environmental stress cracking resistance (Full Notch Creep Test) measured by the internal measurement method described by M. Fleißner in [h], conditions: 95°C , 20 3.5 MPa, water / 2% of Arkopal.

- AFM (-30°C) = notched impact toughness, measured in accordance with ISO 179-1/1eA / DIN 53453 in $[\text{kJ/m}^2]$ at -30°C .

5 - ACN ($+23^{\circ}\text{C}$) = notched impact toughness, measured in accordance with ISO 179-1/1eA / DIN 53453 in $[\text{kJ/m}^2]$ at $+23^{\circ}\text{C}$.

10 An energy cable having a diameter of 5 cm was sheathed externally with the polyethylene molding composition prepared in this way by plasticizing the molding composition at a temperature of 220°C in an extruder and then extruding it through an annular nozzle onto the electric cable and cooling it there. The sheath produced in this way had a thickness of
15 0.5 cm.

The resulting surface on the electric cable was smooth and displayed no visible damage.

20 The electric cable produced in this way was, for test purposes, packed in a steel mesh basket and stored in the River Main in Frankfurt at a depth of 2 m below the water surface. The duration of the storage was 1 year, and the water temperature varied, depending on the time of year, from $+3$ to
25 $+27^{\circ}\text{C}$.

After a storage time of one year, the cable was taken out again and examined visually. After mechanical removal of adhering mud and algae, the appearance of the external
30 sheathing of the cable was no different from the state immediately after it had been produced.

Claims

1. A polyethylene molding composition which has a multimodal molar mass distribution and has a density at a temperature of 23°C in the range from 0.94 to 0.950 g/cm³ and an MFI_{190/5} in the range from 0.5 to 2.1 dg/min and comprises from 45 to 55% by weight of a low molecular weight ethylene homopolymer A, from 30 to 40% by weight of a high molecular weight copolymer B of ethylene and another olefin having from 4 to 8 carbon atoms and from 10 to 20% by weight of an ultra high molecular weight ethylene copolymer C, where all percentages are based on the total weight of the molding composition.
2. The polyethylene molding composition according to claim 1, wherein the high molecular weight copolymer B contains from 1 to 8% by weight, based on the weight of copolymer B, of comonomers having from 4 to 8 carbon atoms and the ultra high molecular weight ethylene copolymer C contains from 1 to 8% by weight, based on the weight of copolymer C, of comonomers.
3. The polyethylene molding composition according to claim 1 or 2 in which 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene or mixtures thereof are present as comonomers.
4. The polyethylene molding composition according to one or more of claims 1 to 3 which has a viscosity number VN_{overall}, measured in accordance with ISO/R 1191 in decalin at a temperature of 135°C in the range from 260 to 340 cm³/g, preferably from 280 to 320 cm³/g.
5. The polyethylene molding composition according to one or more of claims 1 to 4 which has a notched impact toughness

AFM (-30°C) in the range from 3.5 to 4.5 kJ/m² and a notched impact toughness ACN ($+23^{\circ}\text{C}$) in the range from 12 to 16 kJ/m² and has an environmental stress cracking resistance (FNCT) in the range from 150 to 250 h.

5

6. A process for preparing a polyethylene molding composition according to one or more of claims 1 to 5, in which the polymerization of the monomer is carried out in suspension at temperatures in the range from 70 to 90°C, a pressure in the range from 2 to 10 bar and in the presence of a highly active Ziegler catalyst composed of a transition metal compound and an organoaluminum compound, wherein the polymerization is a three-stage polymerization, with the molar mass of the polyethylene formed in each stage being regulated in each case by means of hydrogen.

10

15

7. The process according to claim 6, wherein the hydrogen concentration in the first polymerization stage is set so that the viscosity number VN₁ of the low molecular weight polyethylene A is in the range from 50 to 90 cm³/g.

20

8. The process according to claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is set so that the viscosity number VN₂ of the mixture of polymer A plus polymer B is in the range from 260 to 320 cm³/g.

25

9. The process according to any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is set so that the viscosity number VN₃ of the mixture of polymer A, polymer B plus polymer C is in the range from 260 to 340 cm³/g, in particular from 280 to 320 cm³/g.

30

10. The use of a polyethylene molding composition according to one or more of claims 1 to 5 for the external sheathing of

35

electric cables, wherein the polyethylene molding composition is firstly plasticized in an extruder at temperatures in the range from 200 to 250°C and is then extruded through a nozzle onto the surface of the cable and is cooled there.

5

11. An electric or information transmission cable having an internal, electrically conductive core of metal and an external, electrically nonconductive sheath comprising a polyethylene molding composition according to any of claims 1 to 5, wherein the external sheath has a thickness in the range from 0.2 to 3 cm.

10

15

* * * * *

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L C08F H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 713 561 B1 (BERTHOLD JOACHIM ET AL) 30 March 2004 (2004-03-30) the whole document	1-11
X	WO 2004/058876 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 15 July 2004 (2004-07-15) the whole document	1-11
A	WO 2004/056921 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 8 July 2004 (2004-07-08) the whole document	1-11
A	WO 2004/058878 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 15 July 2004 (2004-07-15) the whole document	1-11

-/--

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

25 April 2006

Date of mailing of the international search report

03/05/2006

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Lippert, S

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	US 6 329 054 B1 (ROGESTEDT LAILA ET AL) 11 December 2001 (2001-12-11) cited in the application the whole document	1-11
A	US 2003/149180 A1 (VAN DUN JOZEF J ET AL) 7 August 2003 (2003-08-07) the whole document	1-11

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6713561	B1	30-03-2004	AT 244264 T 15-07-2003
			AU 769434 B2 29-01-2004
			AU 7001700 A 30-04-2001
			BR 0014232 A 04-06-2002
			CA 2387708 A1 05-04-2001
			CN 1376170 A 23-10-2002
			DE 19945980 A1 29-03-2001
			WO 0123446 A1 05-04-2001
			EP 1228101 A1 07-08-2002
			ES 2200919 T3 16-03-2004
			JP 2003510429 T 18-03-2003
			ZA 200202267 A 15-10-2003
WO 2004058876	A	15-07-2004	AU 2003293791 A1 22-07-2004
			BR 0317322 A 08-11-2005
			CA 2511358 A1 15-07-2004
			EP 1578862 A1 28-09-2005
WO 2004056921	A	08-07-2004	AU 2003293792 A1 14-07-2004
			BR 0316920 A 25-10-2005
			CA 2510063 A1 08-07-2004
			EP 1576047 A1 21-09-2005
WO 2004058878	A	15-07-2004	AU 2003293815 A1 22-07-2004
			BR 0317343 A 08-11-2005
			CA 2511547 A1 15-07-2004
			EP 1576048 A1 21-09-2005
US 6329054	B1	11-12-2001	AU 693784 B2 09-07-1998
			AU 6374896 A 10-02-1997
			BR 9609621 A 06-04-1999
			CA 2225858 A1 30-01-1997
			CN 1190417 A 12-08-1998
			CZ 9800065 A3 15-04-1998
			DE 69604296 D1 21-10-1999
			DE 69604296 T2 06-04-2000
			EP 0837905 A1 29-04-1998
			ES 2138357 T3 01-01-2000
			HU 9802544 A2 29-03-1999
			IN 187867 A1 13-07-2002
			JP 3088467 B2 18-09-2000
			JP 10511734 T 10-11-1998
			PL 324435 A1 25-05-1998
			RU 2137788 C1 20-09-1999
			SE 504455 C2 17-02-1997
			SE 9502508 A 11-01-1997
			WO 9703124 A1 30-01-1997
			TW 411353 B 11-11-2000
			UA 68329 C2 16-08-2004
			ZA 9605857 A 27-01-1997
US 2003149180	A1	07-08-2003	NONE